

## POLYMORPHOUS-CRYSTALLOID NATURE OF VITREOUS AND LIQUID H<sub>2</sub>O

V. S. Minaev\*, S. P. Timoshenkov<sup>a</sup>, S. P. Chernykh<sup>b</sup>

Elma Corp., Research Institute of Material Science and Technology, 124460, Moscow, Russia

<sup>a</sup>Moscow Institute of Electronics Engineering, 124498, Moscow, Russia

<sup>b</sup>Research-Technological Agency "Unisapph", 124460, Moscow, Russia

Based on the concept of polymeric polymorphous-crystalloid (polymeric-polymorphoid) structure of glass and glassforming liquid of individual chemical substances the structure of liquid and vitreous H<sub>2</sub>O has been considered. Experimental data are presented and a number of arguments are suggested which point out that vitreous and liquid water are constructed from structural fragments of crystalline polymorphous modifications (crystalloids or polymorphoids) of H<sub>2</sub>O: ice I, ice II and ice III. Polymorphoids have no long-range order and have an individual intermediate-range order inherent to these polymorphous modifications.

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### 1. Introduction

Problems of glassformation, glass and glassforming liquid structure are still far away from being finally settled. The same can be said about simple glassformers – individual chemical substances (elements and chemical compounds) as well. Among them there is such seemingly simple substance as ubiquitous H<sub>2</sub>O that forms glass, for example, after quenching of droplets of ~ 3 μm dimensions with the rate of >10<sup>5</sup> K.s<sup>-1</sup> on a copper substrate at 77 K [1].

Associated glassforming liquid [2], according to the Tool's kinetic glassformation theory [3], that was further developed in works of other authors analyzed in the Mazurin's monograph [4], is a "precursor" of glass from the structural standpoint and the structural analog of glass taking into account the fictitious (structural) temperature T<sub>f</sub>. Glass science has accumulated a large amount of experimental data in favor of this conclusion that were analyzed in the monographs of Rawson [2] and Minaev [5] as well as in the works [6,7,8]. Therefore, one can draw the conclusion that associated glassforming liquid differs from glass, formed of it, merely in the extent of polymerization of substance. In essence the structure of the former is similar to the structure of the latter at T<sub>f</sub> temperature that characterizes the glass [8]. It follows that data characterizing liquid structure can be attributed (to the great extent of approximation) to glass structure and vice versa. This thesis is especially important in analyzing the structure of vitreous water where the amount of data is significantly less than those for liquid water. The latter are summarized, for example, in the work of Eisenberg and Kauzmann [9]. Some 20 types and subtypes of models of liquid water structure are described in this work. The main of them are as follows:

- models of mixtures that can be divided on
  - a) the model of small aggregates of Chadwell [10] where liquid is considered as an equilibrium mixture of H<sub>2</sub>O, (H<sub>2</sub>O)<sub>2</sub>, (H<sub>2</sub>O)<sub>3</sub> or H<sub>2</sub>O, (H<sub>2</sub>O)<sub>2</sub>, (H<sub>2</sub>O)<sub>4</sub>, (H<sub>2</sub>O)<sub>3</sub>;
  - b) the model of voids where one type of molecules forms a network of hydrogen bonds and another type of molecules is located in voids of the network. There are

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\* Corresponding author: elma@zelmail.ru

- three subtypes of the model: the model of Danford, Levy and Narten [11,12], the Pauling's model of the "water hydrate" [13], the Samoilov's model [14];
- the Pople's model of distorted hydrogen bonds [15];
  - the Bernal's model of an irregular network [16].

Bernal and Fowler [17] criticized the models of small aggregates [10] as giving inadequate description of spatial molecular arrangement in liquid. Having determined that water is described in the better way as expanded but irregular four-coordinated molecules arrangement, they put the foundation of the most known models (Fig. 1).

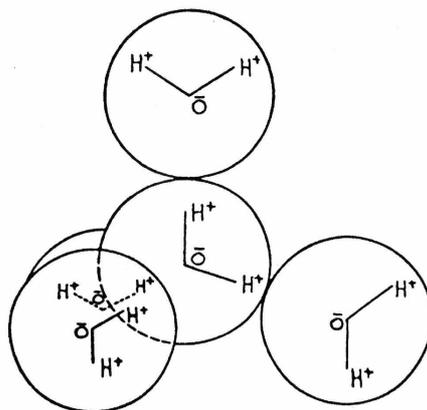


Fig. 1. Tetrahedral coordination of water molecules. The four molecules surrounding one water molecule are shown. Of these, two are in the plane of the paper, one above it and one below it [17].

The goal of this work is to consider structures of liquid and vitreous  $\text{H}_2\text{O}$  from the standpoint of the concept of polymeric polymorphous-crystalloid structure of one-component glass and glassforming liquid proposed by Minaev in 1987 [5-8], in accordance with which glass and liquid are constructed from copolymerized (glass) and non-copolymerized (liquid) structural fragments of different polymorphous modifications (PMs) without a long-range order: crystalloids. The crystalloid is a fragment of crystal structure consisting of a group of atoms, connected by chemical bonds in accordance with rules of stereometric ordering, inherent to one of crystalline PMs of substance and having no translational symmetry of crystal. The crystalloid does not have even minimal long-range order, i.e. two neighboring unit cells of crystal structure capable to inter-translation. The concentration ratio of crystalloids with different structures can change in glass and glassforming liquid depending on conditions of glass production and external conditions in which liquid or glass exist.

The term "crystalloid" used by Graham [18] as long ago as the XIX century with the meaning that is somewhat different from ours, can be replaced with the more exact and so far free term "polymorphoid". In this case the name of the concept becomes simpler. Now it can be called as "the concept of polymeric-polymorphoid structure of glass and glassforming liquid".

Frankenheim (1851)[19], Lebedev (1921) [20,21], Goodman (1975)[22], Wang and Merz (1976)[23], Landa et al. (1979,1984)[24,25], Blinov (1985)[26] have considered that the existence of individual chemical substance (ICS) in different PM types is directly related with glassformation or even it is its main cause. In the process of development of the concept of polymeric-polymorphoid structure of glass [6-8, 27-31] it has been shown by the example of  $\text{SiO}_2$ ,  $\text{GeSe}_2$ ,  $\text{GeS}_2$ ,  $\text{Se}$ ,  $\text{P}_2\text{O}_5$  and other ICS that associated glassforming liquid, as well as glass, is constructed from fragments of different PMs without a long-range order (crystalloids-polymorphoids). Therefore, it was logical to suppose that such glassforming liquid as  $\text{H}_2\text{O}$  and glass, formed from it, also contained polymorphoids of different PMs.

Crystalline  $\text{H}_2\text{O}$  (ice) exists in 12 polymorphous modifications, the first of which, ice I, has two types – hexagonal ice  $\text{I}_h$  and cubic ice  $\text{I}_c$ . Fig. 2 shows the phase diagram of water adopted from Pauling's monograph [32]. A similar diagram is shown in the work [9]. Its legend says that the

diagram is based on data of Bridgeman [33-35], Brawn and Walley [36] and that the figure itself is taken in a modified kind from the Kamb's work [37].

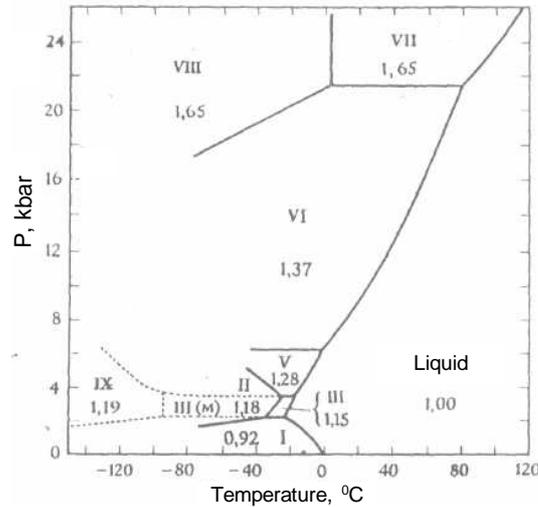


Fig. 2. Phase diagram of water where regions of stable existence of different ice types (they are designated by Roman numerals) and liquid water are shown. For each phase is shown the approximate density ( $\text{g}\cdot\text{cm}^{-3}$ ) providing stability at the lowest pressure. The region III(m) corresponds to the metastable state of ice III in super-cooled state; stable in this region is ice II [32].

On the diagram presented there are no three later revealed crystalline H<sub>2</sub>O modifications: ice X, obtained from ice VII at the pressure of 44000 MPa and temperature of 300 K (1984)[38], ice XI, obtained at the pressure of 150 MPa and temperature lower 300 K (1985)[39], and ice XII, located below the line (temperature) connecting points 90 K at 1200 MPa and 120 K at 2150 MPa [40,41]. Some characteristics of several crystalline PMs are presented in Table 1.

Table 1. Characteristics of polymorphous types of ice [9].

Type of ice	I <sub>h</sub>	I <sub>c</sub>	II	III	V	VI	VII	VIII
Crystal system	Hexagonal	Cubic	Rhombo-hedral	Tetragonal	Monoclinic	Tetragonal	Cubic	Cubic
Density at -175 °C and 1 atm., $\text{g}/\text{cm}^3$	0.94		1.17	1.14	1.23.	1.31		1.50
Density ( $\text{g}/\text{cm}^3$ ) at t °C; P kBar) in the stability region)	0.92 (0°; 1)	0.93 (-130°; 1)	1.18 (-35°; 2.1)	1.15 (-22°; 2.0)	1.26 (-5°; 5.3)	1.31 (15°; 8)	1.65 (25°; 25)	1.66 (-50°; 25)
Distances between nearest molecules, Å	2.74	2.75	2.75-2.81	2.76-2.80	2.76-2.87	2.81	2.86	2.86
Distance to the nearest molecule, not connected with hydrogen bond, Å	4.49	4.50	3.24	3.47	3.28; 3.46	3.51	2.86	2.86
Angles O...O...O	109.5±0.2	109.5	80-128	87-141	84-135	76-128	109.5	109.5
Positions of hydrogen atoms	Random	Random	Ordered	Random higher than -40 °C	Random	Random	Random	Ordered

## 2. Consideration of structural models of liquid H<sub>2</sub>O by Pople and Bernal from the standpoint of the concept of polymeric-polymorphoid glass structure

To justify the appropriateness of the supposition on the construction of vitreous and liquid water from copolymerized (glass) and non-connected (liquid) crystalloids of different PMs, let us consider the main models of liquid H<sub>2</sub>O structure in more detail.

Models of voids like small aggregates models were “excoriated” [9], so among “working” models well correlating with X-ray data there remain similar models of distorted hydrogen bonds of Pople [15] and the irregular network of Bernal [16].

Pople [15] has developed a model of liquid water where the majority of hydrogen bonds were considered as distorted but not broken. Distances from the central molecule to secondary ones (i.e. following after nearest neighbors), tertiary ones, etc. will be dependent on the extent of bending of the hydrogen bond. The hydrogen bond is not bent if the group O-H of one of molecules and the unshared electron pair of the oxygen atom of the neighboring molecule, participating to the formation of the hydrogen bond, lie along the line “oxygen-oxygen” of two molecules (Fig. 1). In other words, the energy of bending of the hydrogen bond is equal to zero when all angles H<sub>2</sub>O..... H<sub>2</sub>O..... H<sub>2</sub>O are tetrahedral ones like ice I. When the direction of the unshared electron pair deviates from the line “oxygen-oxygen” on the angle  $\varphi$  (Fig. 3), the hydrogen bond becomes bent and the energy of the system increases to the value

$$\Delta U = k_{\varphi} (1 - \cos \varphi) \quad (1)$$

where  $k_{\varphi}$  - the constant of the bending force of the hydrogen bond.

By varying the number of neighboring molecules, bending force constants of hydrogen bonds and parameters of the Gaussian distribution of first neighbours, Pople came to the good correspondence with experimental distribution functions [40]. Pople calculated the average angle of the hydrogen bond distortion  $\varphi$ :  $-26^{\circ}$  and  $30^{\circ}$  at  $0^{\circ}\text{C}$  and  $100^{\circ}\text{C}$ , correspondingly.

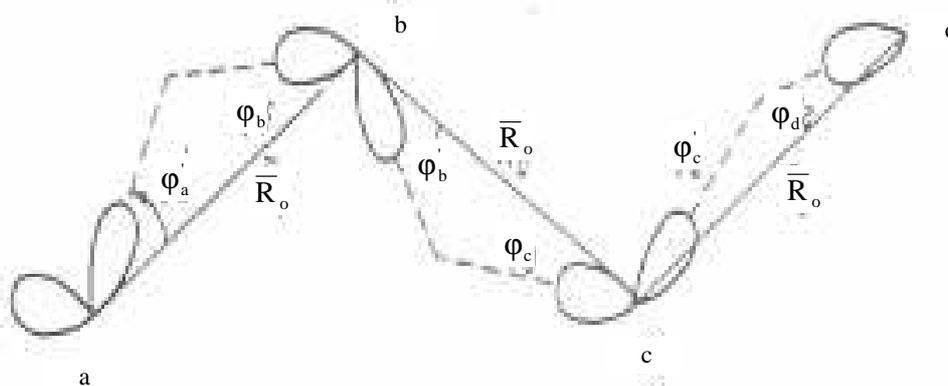


Fig. 3. Bending of hydrogen bonds according to Pople. *a* – the central molecule, *b* – the nearest neighboring molecule, *c* – the secondary neighboring molecule, *d* – the tertiary neighboring molecule. Each lobe designates either the bond O – H or the unshared pair of electrons. Angles  $\varphi_i$  characterize the extent of bending of bonds. Distances to neighbors  $\bar{R}_o$  are constant [15].

However, the Pople’s model does not explain the small peak at  $3.5 \text{ \AA}$  in the radial distribution function. Besides, some authors raised objections against his model, contending that liquid with such developed system of hydrogen bond would be very viscous; although, from another side, the standpoint was expressed that there was not a big difference between broken and strongly distorted hydrogen bonds in liquid water [9].

The main idea of the Pople's concept does not contradict the concept of polymeric-polymorphoid structure of glass and glassforming liquid [6,7,22]. Actually, according to this concept, associated glassforming liquid is an assembly of structural fragments of different polymorphous modifications of the given ICS, practically unconnected at high temperatures and gradually copolymerizing with temperature decrease. In the case of water they are structural fragments of some of its PMs. According to Camb's data [41], in the PM ice II hydrogen bonds are bended in average on the angle  $\phi$  equal to  $8^\circ$ ; in PMs ice I<sub>h</sub> and I<sub>c</sub> equilibrium angles of bonds O...H-O are deviated from  $180^\circ$  on  $7^\circ$  maximum [9]. PMs ice III, V and VI also contain distorted hydrogen bonds. If water consists of structural fragments (polymorphoids) of several PMs, it obviously contains several varieties of distorted hydrogen bonds that corresponds to the Pople's model. And, at the same time, the Minaev's concept, unlike the Pople's concept, leaves wide possibilities for alterations of viscosity of liquid depending on its temperature and the extent of copolymerization of fragments with different structures preventing crystallization of liquid into one of PMs [6-8].

The model, proposed by Bernal [16,17], presents a random network from connected by hydrogen bonds tetra-coordinated molecules, forming rings with 4, 5, 6, 7 and more molecules in rings. The largest number of molecules contains 5-member rings because the angle of the bond H-O...H between water molecules is equal approximately to  $108^\circ$ , i.e. the angle in the 5-member ring.

At the same time, it is known that in different PMs of ice there are 4-, 5-, 6- and 8-member rings present [9]. It means that the irregular network of vitreous can consist of polymorphoids of different PMs that actually makes the Bernal's and Minaev's concepts very similar. The similarity of these concepts becomes even greater taking into account that the irregular network of Bernal's rings leads to appearance of one, or possibly several, small peaks in the radial distribution function in intervals between big peaks  $\approx 2, 9$  and  $4.5 \text{ \AA}$ . These peaks are the result of at least two types of configuration: 4-member rings, revealed in ice VI, and superposition of two 6-member rings with the bending of hydrogen bonds analogous to that in ice II [9]. The presence in water of configurations, which are similar to the tridimite structure typical for ice I<sub>h</sub>, and quartz-like or keatite-like configurations of the molecules arrangement in water was shown by Bernal in [16,17]. We can see that the idea of polymorphous structure of one of types of liquid was presented in the implicit form in the Bernal's concept as long ago as 1933 [16], i.e. even before Burton and Oliver revealed vitreous ice in 1936 [42]. In 1964 Bernal [17] suggested that his model of the irregular network consisted of rings with different numbers of water molecules was apparently correct for glasses.

Models of Pople [15] and Bernal [16,17] are very similar: Bernal's rings contain, like in the Pople's model, distorted hydrogen bonds. Both models, in their essence, are based on the concept of polymeric-polymorphoid structure of glass and glassforming liquid of ICS. And the latter concept combines and expands the structural notions by using the idea of a different (depending on external conditions) extent of copolymerization and concentration ratio of structural fragments (polymorphoids) of different PMs without a long-range order which include rings with distorted and undistorted chemical bonds. Besides, the new concept brings strictly determined intermediate ordering into a continuous random network – each type of polymorphoid has its own intermediate-range order, inherent to only its crystalline polymorphous modification. Just co-existence of polymorphoids of different PMs is the main cause of the existence of glass.

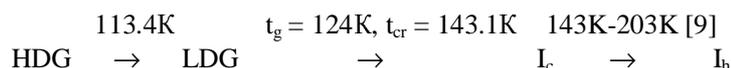
### 3. Some features of vitreous water

Ideas of Pople [15], Bernal [16,17], Minaev [6-8,28] well agree with calculated and experimental data on vitreous water presented in works of Popescu [45] and Narten et al. [46].

But, firstly, we present some general information on vitreous ice. There are two types of vitreous water or vitreous ice: low-density glass (LDG) and high-density glass (HDG). LDG can exist at temperatures below  $T_g$  ( $\sim 130 \text{ K}$ ) at pressure of 1 atm. [47]. LDG is obtained by vapor deposition on a cold substrate, extremely fast ( $> 10^5 \text{ K}\cdot\text{s}^{-1}$ ) cooling of micron-size droplets [1,48] and directly from HDG in accordance with the reversible reaction  $\text{HDG} \rightleftharpoons \text{LDG}$  [47,49]. The density of LDG is  $0.93 \text{ g}\cdot\text{cm}^{-3}$  [50] that is just slightly greater than the density of ice I<sub>h</sub> ( $0.92 \text{ g}\cdot\text{cm}^{-3}$ ) [9]. HDG (density  $1.1 \text{ g}\cdot\text{cm}^{-3}$ ) was apparently obtained for the first time by Narten et al. in 1976 [46] by vapor deposition at 10 K. It can be also obtained by compression of ice I<sub>h</sub> at temperature below 150 K, by

bombardment of  $I_h$  with an electron beam, and from LDG in accordance with the reversible reaction  $LDG \rightleftharpoons HDG$  taking place at pressure of  $\sim 0.2$  GPa and temperature of 130-150 K. HDG can be quenched at pressure of 1 atm. at temperatures below 120 K [49].

Handa et al. [51,52] has revealed phase transformations  $HDG \rightarrow LDG$  (113.4 K,  $-544 \text{ J.mole}^{-1}$ ),  $LDG \rightarrow I_c$  (143.1 K,  $-1424 \text{ J.mole}^{-1}$ ),  $I_c \rightarrow I_h$  ( $-35,5 \text{ J.mole}^{-1}$ ). The glass transition temperature of LDG is 124 K (after annealing of samples at 124-130 K) \*



#### 4. Model of vitreous water developed by Popescu

In the work of Popescu [45] simulation of solid vitreous water was carried out using hand-made models and the procedure of computer relaxation. The LDG structure was reproduced as a model of continuous random network of tetrahedral packed water molecules forming 5-, 6-, 7- and 8-member rings of oxygen atoms (31%, 44%, 22% and 4%, correspondingly) with small amount of 4-member rings. The HDG structure was reproduced as a model containing only 6- and 8-member rings (76% and 24%, correspondingly). Van-der-Vaals forces between oxygen atoms were taken into account in this model.

The structural factor and the reduced radial distribution function, calculated by Popescu, well agree with experimental ones for LDG samples obtained by vapor deposition at 77 K and HDG samples obtained at 10K [46]. Calculated and experimental densities also well agree: 0.89 and  $0.93 \text{ g.cm}^{-3}$  for LDG (the model and the experiment, correspondingly) and 1.08 and  $1.10 \text{ g.cm}^{-3}$  for HDG (the model and the experiment, correspondingly).

Presence of above shown rings, formed from  $\text{H}_2\text{O}$  molecules, in structures of vitreous types of ice [45] that are the same as those in its crystalline PMs, as well as density values that are intermediate between those of crystalline PMs (see Table), are arguments in favor of applicability of the polymeric-polymorphoid structure concept to liquid and vitreous water. These arguments were well established in the case of vitreous  $\text{SiO}_2$  [6].

#### 5. Reversible process of glass transition and inter-transformation of polymorphoids of different PMs

The important argument in favor of polymorphoid structure of vitreous water is the existence of the glass transition temperature. In the papers [6,27] it is clearly shown by the example of  $\text{SiO}_2$ ,  $\text{GeSe}_2$ ,  $\text{GeO}_2$ , Se and others that  $T_g$  is the temperature of the most active stage of transformation of polymorphoids of one PM into polymorphoids of another PM,  $T_g$  in glass is an analog of the polymorphous transformation temperature in crystalline substance.

In the work of Yohari et al. [1] it is said that in early carried out investigations of vitreous  $\text{H}_2\text{O}$  the transition "glass-liquid" at heating was not revealed and experimental data, based on differential scanning calorimetry, are presented demonstrating reversibility of this transition in the temperature range of 113-148 K with well expressed glass transition temperature. In experimental conditions, described in the legend of Fig. 4, the glass transition temperature  $T_g$  equal to  $136 \pm 1 \text{ K}$ , the midpoint temperature of glass-transition region  $T_{mdp}$  equal to  $142 \pm 1 \text{ K}$  and ice crystallization temperature  $I_c$  equal to  $150 \pm 1 \text{ K}$  were determined.

Sharp decrease of heat capacity of a glass sample is observed on the curve 1 up to 130 K. The exothermal effect is observed here that was not explained by authors. Curves 2 and 3 were obtained after annealing of the sample at 130 K, cooling it to 103 K and reheating. As it is seen on the figure,

\* Data on  $T_g$  and annealing temperature do not match: heating of glass higher  $T_g$  must lead to formation of supercooled liquid and its subsequent crystallization. Apparently, authors [51,52] annealed glass at temperature below  $T_g$ .

the exothermic effect is not observed, but the endothermic effect of glass transition (glass softening) is observed instead in the interval 136-150 K – the curve 3.

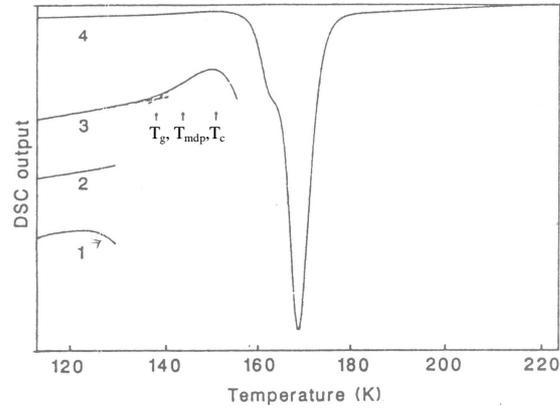


Fig. 4. The DSC scans of the hyperquenched glassy water (prepared by using a 300  $\mu\text{m}$  aperture) taken during heating at 30  $\text{K min}^{-1}$ . Curve 1 is for 17.7 mg sample heated to 130 K. Curve 2 is for the same sample, but after annealing for 95 min at 130 K, cooled to 103 K and heated to 130 K. Curve 3 is for the same sample which was cooled from 130 K to 103 K and again heated to 283 K. Curve 4 is the same as curve 3, but plotted on a reduced scale ( $1/8^{\text{th}}$ ) to show the crystallization peak of glassy water to cubic ice.  $T_g$  is the glass transition temperature,  $T_{\text{mdp}}$  is the mid-point temperature, and  $T_c$  is the crystallization temperature, all corresponding to 30  $\text{K}\cdot\text{min}^{-1}$  heating rate. The temperature axis is not corrected for the thermal lag of the instrument [1].

Fig. 5 presents the results of the experiment showing reversibility of the glass transition process during the thermal cycle. In this cycle a hyper-quenched sample was brought to the state of super-cooled liquid at 148 K (the curve 3 on Fig. 5), then sharply ( $200 \text{ K}\cdot\text{min}^{-1}$ ) quenched at 103 K, then heated to 130 K and annealed at this temperature during 1 hour. Then the sample was cooled to 103 K again and finally the differential scanning was carried out that showed (curve 4) the repeated glass transition process.

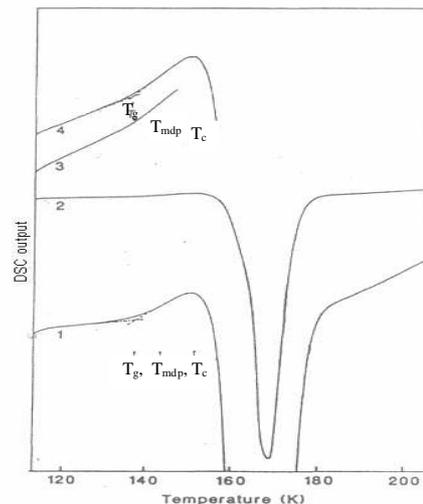


Fig. 5. The DSC scans of the hyperquenched glassy water prepared by using a 200  $\mu\text{m}$  aperture. Curve 1 is for a 26.9 mg sample annealed at 130 K for 4 h, cooled to 103 K and heated, Curve 2 is the same as curve 1, but plotted on a reduce scale ( $1/8^{\text{th}}$ ). Curve 3 is for a 15.5 mg sample annealed at 130 K for 1.5 h and heated to 148 K. Curve 4 is for the same sample which was cooled immediately after curve 3 from 148 K to 103 K at a rate of 200  $\text{K}\cdot\text{min}^{-1}$  while inside the calorimeter, then heated to 130 K, annealed for 1 h at 130 K, again cooled to 103 K, and finally heated for the DSC scan. The notations are the same as in Fig. 3 [1].

Authors of the work [1] did not explain the physical-chemical mechanism of processes taking place in the cycling process and in the annealing process at 130 K that was necessary for subsequent fixation of the glass softening process and its temperature  $T_g$ .

From the standpoint of the concept of polymeric-polymorphoid structure of glass and glassforming liquid [6-8,27,28], both glass and glassforming liquid are constructed from polymorphoids, without a long-range order, of at least two polymorphous modifications (in this case – ice modifications) that prevents their crystallization in certain conditions. At temperatures below  $T_g$  low-temperature PM (LTPM) is stable, at temperatures higher  $T_g$  high-temperature PM (HTPM) is stable. The latter is metastable at temperatures lower  $T_g$ . In crystalline state LTPM and HTPM undergo the reversible (enantiotropic) polymorphous transformation. In vitreous state or in state of super-cooled liquid, where polymorphoids of both modifications are present, at temperatures higher  $T_g$  the process of polymorphoid transformation LTPM  $\rightarrow$  HTPM is taking place and at temperatures lower  $T_g$  the reverse process is taking place.

The reverse process goes slower due to lower temperature and significant time is needed for transformation of all HTPM polymorphoids into LTPM polymorphoids, i.e. for crystallization of glass as LTPM. At temperatures higher  $T_g$  LTPM polymorphoids become destroyed, glass become softened, more HTPM polymorphoids are formed, and finally there are so many of them that formed super-cooled liquid is crystallized as HTPM. In our case, it is  $I_c$  (curve 2, Fig. 5).

At melting of HTPM, polymorphoids of this PM go from solid state into liquid state. But already from the initial moment of melting, some amount of polymorphoids of other PMs, LTPM in particular, are formed which hinder the process of HTPM crystallization during cooling of liquid. In the case of water, at cooling it from 4 °C to 0 °C, the number of LTPM polymorphoids sharply decreases and, therefore, high cooling rate is needed for the process of glass transition. As the result, at scanning of such glass it is very difficult to observe during heating the polymorphoid transformation LTPM  $\rightarrow$  HTPM, i.e. the endothermal peak and  $T_g$ , because the portion of LTPM in glass is too small. But if glass is annealed at temperatures, slightly lower than  $T_g$  ( $\approx 130$  K), and, as the result the polymorphoid transformation HTPM  $\rightarrow$  LTPM, glass becomes enriched with the latter at the expense of the former. As the result, heating glass after annealing, the polymorphoid transformation process LTPM  $\rightarrow$  HTPM intensifies that is fixed as the endothermal effect, the effect that is observed for the polymorphous transformation in crystalline substance at heating as well.

The described mechanism of the transformation LTPM  $\rightleftharpoons$  HTPM demonstrates itself at heating of glass as a sequence of thermal effects: exothermic (transformation of polymorphoids “HTPM  $\rightarrow$  LTPM”) – lower  $T_g$ , endothermic (transformation of polymorphoids “LTPM  $\rightarrow$  HTPM”) – at and higher  $T_g$ , and again exothermic (crystallization of HTPM). The same effects become also apparent at heating of glasses GeSe<sub>2</sub>, AsSe [6,8] and other ICS with enantiotropic polymorphous transformations. The temperature of this phase transformation in crystal line substance is transmuted into the temperature of the structural transformation of polymorphoids LTPM  $\rightleftharpoons$  HTPM in vitreous substance and is registered as the glass transition temperature (at cooling) or as the softening temperature (at heating) [28].

No other concept but only the concept of polymeric-polymorphoid structure of glass and glassforming liquid could explain satisfactorily, the physical-chemical essence of annealing, softening and glass transition processes.

Which ice polymorphous modifications take part in the above processes? It is obvious that polymorphoids of high-temperature PM are structural fragments of ice  $I_h$ . What about low-temperature ice? Unfortunately, there is no clear answer to this question. The phase diagram of water (Fig. 2) in the low temperature range for pressure of one atmosphere is not yet completed. Nevertheless, it is clearly seen on the diagram that the border between regions of ice I and ice II, that was constructed only to temperature of  $\sim 200$  K, is directed to lower pressures. If we conceptually continue this border, it could reach the pressure coordinate of 1 atmosphere in the range between 120-140 K, i.e. in the range of  $T_g$ . Therefore, beginning from these temperatures, ice II can exist at atmospheric pressure. It means that ice II can be low-temperature PM at atmospheric pressure. It is necessary to note that ice III in metastable state, that borders are not determined exactly, also exists in the range of existence of ice II as well as the low-temperature type of ice III with regularly arranged

protons – ice IX. So, we have three candidates for LTPM which polymorphoids, contained in glass, are transformed into HTPM polymorphoids, i.e. ice I polymorphoids, in the range of  $T_g$ .

And where polymorphoids of ice II and ice III appear from in vitreous water? The only source for them is liquid water. In the work [32] Pauling writes that the transition ice I  $\rightarrow$  H<sub>2</sub>O (liquid) is accompanied by the enthalpy change  $\Delta H^\circ = 6.0 \text{ kJ.mole}^{-1}$  that can be explained by breakage of some hydrogen bonds or their deformation as, for example, in the case of ice II. He assumes that both these processes are characteristic for liquid water. The X-ray diagram of liquid water at 4 °C well agrees with the diagram calculated for the mixture of micro-crystals of ice I<sub>h</sub>, ice II and ice III in the ratio 50:33:17. Pauling assumes that the surroundings of each molecule in water deviate from those in ice I<sub>h</sub> and are closer to those in ice II and ice III. He adds: the density of liquid water ( $1 \text{ g.cm}^{-3}$ ) is intermediate between densities of ice I ( $0.92 \text{ g.cm}^{-3}$ ), ice II ( $1.18 \text{ g.cm}^{-3}$ ) and ice III ( $1.15 \text{ g.cm}^{-3}$ ).

The facts presented above completely agree with the concept of polymeric- polymorphoid structure of glass and glassforming liquid and allow to draw the conclusions below.

## 6. Conclusions

1) Using the examples of structural transformations in liquid, supercooled and vitreous water, it was shown that the concept of polymeric-polymorphoid structure of glass and glassforming liquid allows for interpreting the earlier unexplained experimental data.

2) The concept of polymeric-polymorphoid structure of glass and glassforming liquid includes (in the modified form) Pople's and Bernal's structural models of liquid water and Popescu's structural model of vitreous water. It combines them and expands by introducing in them the notions of structure of liquid and vitreous water with the idea of different (depending on external conditions) extent of co-polymerization and concentration ratio of structural fragments of different polymorphous modifications (polymorphoids), without a long-range order but with an individual intermediate-range order, containing rings with distorted and undistorted bonds.

3) This concept allows to predict with high reliability that

- in liquid water, besides ice I polymorphoids, polymorphoids of ice II and ice III appear at melting of ice I<sub>h</sub>, which concentration reaches the maximum at 4 °C and sharply decreases when the temperatures down to decrease to 0 °C;

- the mixture of polymorphoids with different structures, presenting ice I, ice II and ice III (or IX), forms glass at fast cooling of water;

- heating of glass leads to transformations of LTPM polymorphoids (ice II and ice III) into HTPM polymorphoids, i.e. to formation of ice I, at cooling of supercooled liquid or in the process of annealing of glass at temperatures slightly less than  $T_g$  the reverse process takes place – formation of LTPM polymorphoids from HTPM polymorphoids.

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